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Reinforced coatings with improved scratch resistance

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Reinforced coatings with improved scratch resistance

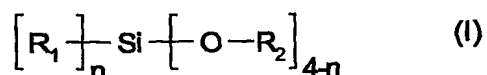
The present invention relates to coating compositions comprising an organic film-forming binder, preferably a coating material, and an inorganic additive of small particle size dispersed in an aqueous or alcoholic solvent to the use thereof in coating compositions as reinforcer of coatings and improver of scratch resistance in coating compositions for surfaces.

Organic coatings are generally susceptible to damages by abrasion and by scratching. Inorganic additives such as metal oxides are hard materials and can be used to reinforce coatings, thus increasing their resistance towards damages. A disadvantage of inorganic additives is, however, their low transparency of visible light. This may induce opacity or an undesired color shift of the substrate. This disadvantage can be circumvented when the inorganic additives are small enough not to interfere with visible light, that is, below a given size, light diffraction can be suppressed. The preparation of small inorganic particles has been described, for example by Stöber, Fink and Bohn [*J. Colloid Interface Sci.* **1969**, 26, 62]. The smaller particles are, the more they tend to agglomerate and aggregate. This tendency must be suppressed in order to achieve the anticipated beneficial results. Generally, agglomeration is suppressed by functionalising the particles, for example by modifying the surface of particles with a reactive group that shows high compatibility with the matrix system, for example the coating. In fact, it has been noted that surface modifications are essential to achieve advantageous effects.

It has been found a process and a composition, which is based on the use of inorganic additives in order to reinforce coatings. Surprisingly the inorganic particles do not essentially need to be modified at their surface in order to show good compatibility with coatings components. Also remarkably, these coatings show significantly increased scratch resistance after curing already at low additive concentrations, when compared with coatings that have not been treated with such inorganic additives. Finally, the addition of small quantities of additives according to our procedure unexpectedly improves the initial gloss of the coating. This effect provides a further advantage of our technology.

The invention therefore relates to coating compositions comprising

- a) an organic film-forming binder, and
- b) an inorganic additive of small particle size dispersed in an aqueous or alcoholic solvent prepared by a process which comprises the hydrolysis of a metal alcoholate, metal halide or a compound of the formula I



in which

R_1 is C_1 - C_8 alkyl, C_5 - C_8 cycloalkyl, phenyl or C_1 - C_4 alkyl substituted phenyl;

R_2 is C_1 - C_8 alkyl, and

n is 0, 1, 2 or 3; with a base.

Alkyl having up to 8 carbon atoms is a branched or unbranched radical such as, for example, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-ethyl-butyl, n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl or 2-ethylhexyl.

C_5 - C_8 cycloalkyl is for example cyclopentyl, cyclohexyl, cycloheptyl or cyclooctyl. Preference is given to cyclohexyl.

C_1 - C_4 Alkyl-substituted phenyl, which contains preferably from 1 to 3, especially 1 or 2, alkyl groups, is, for example, o-, m- or p-methylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2,5-dimethylphenyl, 2,6-dimethylphenyl, 3,4-dimethylphenyl, 3,5-dimethylphenyl, 2-methyl-6-ethylphenyl, 4-tert-butylphenyl, 2-ethylphenyl or 2,6-diethylphenyl.

Of special interest are transparent coating compositions which after curing lead to transparent coatings.

Preferably the metal in the metal alcoholates and metal halides are beryllium, aluminium, titanium, chromium, iron, zinc, zirconium, niobium or cerium.

Halides are for example fluorides, chlorides, bromides or iodides.

Preferably the alcoholic solvent is methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol or tert-butanol or mixtures thereof.

Of interest are coating compositions in which the base is an aqueous base.

Of special interest are coating compositions in which the base is an amine of the formula II



wherein

R₃, R₄ and R₅ independently of one another are hydrogen or C₁-C₈alkyl.

Preferably the particle size of component (b) [inorganic additive] is in the range of from 2 to 300 nanometre.

Of interest are coating compositions wherein in the preparation of component (b) the hydrolysis takes place at a temperature range of from -20 to 80°C, especially -10 to 50°C, for example 10 - 25°C.

Of special interest are compositions wherein in the compound of the formula I n is 0.

Particular mention is to be made of coating compositions in which component (b) is a hydrolyzed compound of the formula I wherein, R₂ is ethyl, and n is 0, with aqueous ammonia.

The starting materials for the preparation of component (b) like for example the metal alcoholates, metal halides or the compounds of the formula I are known in the literature and most of them commercially available at Fluka or Aldrich.

The coating composition is preferably a coating material or paint, especially an aqueous coating material or an aqueous paint.

Examples of coating materials are lacquers, paints or varnishes. These always contain an organic film-forming binder in addition to other, optional components.

Preferred organic film-forming binders are epoxy resins, polyurethane resins, amino resins, acrylic resins, acrylic copolymer resins, polyvinyl resins, phenolic resins, styrene/butadiene copolymer resins, vinyl/acrylic copolymer resins, polyester resins, UV-curable resins or alkyd resins, or a mixture of two or more of these resins, or an aqueous basic or acidic dispersion of these resins or mixtures of these resins, or an aqueous emulsion of these resins or mixtures of these resins.

Of particular interest are organic film-forming binders for aqueous coating compositions, such as, for example, alkyd resins; acrylic resins, two-component epoxy resins; polyurethane resins; polyester resins, which are usually saturated; water-dilutable phenolic resins or derived dispersions; water-dilutable urea resins; resins based on vinyl/acrylic copolymers; and hybrid systems based on, for example, epoxy acrylates.

More specifically, the alkyd resins can be water-dilutable alkyd resin systems which can be employed in air-drying form or in the form of stoving systems, optionally in combination with water-dilutable melamine resins; the systems may also be oxidatively drying, air-drying or stoving systems which are optionally employed in combination with aqueous dispersions based on acrylic resins or copolymers thereof, with vinyl acetates, etc.

The acrylic resins can be pure acrylic resins, epoxy acrylate hybrid systems, acrylic acid or acrylic ester copolymers, combinations with vinyl resins, or copolymers with vinyl monomers such as vinyl acetate, styrene or butadiene. These systems can be air-drying systems or stoving systems.

In combination with appropriate polyamine crosslinkers, water-dilutable epoxy resins exhibit excellent mechanical and chemical resistance. If liquid epoxy resins are used, the addition of organic solvents to aqueous systems can be omitted. The use of solid resins or solid-resin dispersions usually necessitates the addition of small amounts of solvent in order to improve film formation.

Preferred epoxy resins are those based on aromatic polyols, especially those based on bisphenols. The epoxy resins are employed in combination with crosslinkers. The latter may in particular be amino- or hydroxy-functional compounds, an acid, an acid anhydride or a Lewis acid. Examples thereof are polyamines, polyaminoamides, polysulfide-based polymers, polyphenols, boron fluorides and their complex compounds, polycarboxylic acids, 1,2-dicarboxylic anhydrides or pyromellitic dianhydride.

Polyurethane resins are derived from polyethers, polyesters and polybutadienes with terminal hydroxyl groups, on the one hand, and from aliphatic or aromatic polyisocyanates on the other hand.

Preferably, the polyurethanes are prepared in situ from polyethers, polyesters and polybutadienes with terminal hydroxyl groups, on the one hand, and from aliphatic or aromatic polyisocyanates on the other hand.

Examples of suitable polyvinyl resins are polyvinylbutyral, polyvinyl acetate or copolymers thereof.

Suitable phenolic resins are synthetic resins in the course of whose construction phenols are the principal component, i.e. in particular phenol-, cresol-, xylene- and resorcinol-formaldehyde resins, alkylphenolic resins, and condensation products of phenols with acetaldehyde, furfural, acrolein or other aldehydes. Modified phenolic resins are also of interest.

UV-(ultraviolet) curable resins may contain one or more olefinic double bonds. They may be of low (monomeric) or relatively high (oligomeric) molecular mass. Examples of monomers containing a double bond are alkyl or hydroxyalkyl acrylates or methacrylates, such as methyl, ethyl, butyl, 2-ethylhexyl or 2-hydroxyethyl acrylate, isobornyl acrylate, methyl methacrylate or ethyl methacrylate. Other examples are acrylonitrile, acrylamide, methacrylamide, N-substituted (meth)acrylamides, vinyl esters such as vinyl acetate, vinyl ethers such as isobutyl vinyl ether, styrene, alkylstyrenes and halostyrenes, N-vinylpyrrolidone, vinyl chloride or vinylidene chloride.

Examples of monomers containing two or more double bonds are ethylene glycol, propylene glycol, neopentyl glycol, hexamethylene glycol and bisphenol A diacrylates, 4,4'-bis(2-acryl-

oxyethoxy)diphenylpropane, trimethylolpropane triacrylate, pentaerythritol triacrylate or tetraacrylate, vinyl acrylate, divinylbenzene, divinyl succinate, diallyl phthalate, triallyl phosphate, triallyl isocyanurate or tris(2-acryloylethyl) isocyanurate.

Examples of relatively high molecular mass (oligomeric) polyunsaturated compounds are acrylated epoxy resin and acrylated or vinyl ether- or epoxy-functional polyesters, polyurethanes and polyethers. Further examples of unsaturated oligomers are unsaturated polyester resins, generally prepared from maleic acid, phthalic acid and one or more diols and having molecular weights of from about 500 to 3000. In addition to these it is also possible to use vinyl ether monomers and oligomers, and also maleate-terminated oligomers with polyesters, polyurethane, polyether, polyvinyl ether and epoxide main chains. Especially suitable are combinations of polymers and oligomers which carry vinyl ether groups, as described in WO-A-90/01512. Also suitable, however, are copolymers of monomers functionalized with maleic acid and vinyl ether.

Also suitable are compounds containing one or more free-radically polymerizable double bonds. In these compounds the free-radically polymerizable double bonds are preferably in the form of (meth)acryloyl groups. (Meth)acryloyl and, respectively, (meth)acrylic here and below means acryloyl and/or methacryloyl, and acrylic and/or methacrylic, respectively. Preferably, at least two polymerizable double bonds are present in the molecule in the form of (meth)acryloyl groups. The compounds in question may comprise, for example, (meth)acryloyl-functional oligomeric and/or polymeric compounds of poly(meth) acrylate. The number-average molecular mass of this compound may be for example from 300 to 10 000, preferably from 800 to 10 000. The compounds preferably containing free-radically polymerizable double bonds in the form of (meth)acryloyl groups may be obtained by customary methods, for example by reacting poly(meth)acrylates with (meth)acrylic acid. These and other preparation methods are described in the literature and are known to the person skilled in the art. Unsaturated oligomers of this kind may also be referred to as prepolymers.

Functionalized acrylates are also suitable. Examples of suitable monomers which are normally used to form the backbone (the base polymer) of such functionalized acrylate and methacrylate polymers are acrylate, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, n-butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate etc. Additionally, appropriate

amounts of functional monomers are copolymerized during the polymerization in order to give the functional polymers. Acid-functionalized acrylate or methacrylate polymers are obtained using acid-functional monomers such as acrylic acid and methacrylic acid. Hydroxy-functional acrylate or methacrylate polymers are formed from hydroxy-functional monomers, such as 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate and 3,4-dihydroxybutyl methacrylate. Epoxy-functionalized acrylate or methacrylate polymers are obtained using epoxy-functional monomers such as glycidyl methacrylate, 2,3-epoxybutyl methacrylate, 3,4-epoxybutyl methacrylate, 2,3-epoxycyclohexyl methacrylate, 10,11-epoxyundecyl methacrylate etc. Similarly, for example, isocyanate-functionalized polymers may be prepared from isocyanate-functionalized monomers, such as meta-isopropenyl- α,α -dimethylbenzyl isocyanate, for example.

Particularly suitable compounds are, for example, esters of ethylenically unsaturated mono-functional or polyfunctional carboxylic acids and polyols or polyepoxides, and polymers containing ethylenically unsaturated groups in the chain or in side groups, such as unsaturated polyesters, polyamides and polyurethanes and copolymers thereof, alkyd resins, polybutadiene and butadiene copolymers, polyisoprene and isoprene copolymers, polymers and copolymers containing (meth)acrylic groups in side chains, and also mixtures of one or more such polymers.

Examples of suitable monofunctional or polyfunctional unsaturated carboxylic acids are acrylic acid, methacrylic acid, crotonic acid, itaconic acid, cinnamic acid, maleic acid, fumaric acid, unsaturated fatty acids such as linolenic acid or oleic acid. Acrylic acid and methacrylic acid are preferred.

It is, however, also possible to use saturated dicarboxylic or polycarboxylic acids in a mixture with unsaturated carboxylic acids. Examples of suitable saturated dicarboxylic or polycarboxylic acids include tetrachlorophthalic acid, tetrabromophthalic acid, phthalic acid, trimellitic acid, heptanedicarboxylic acid, sebacic acid, dodecanedicarboxylic acid, hexahydrophthalic acid, etc.

Suitable polyols include aromatic and especially aliphatic and cycloaliphatic polyols. Preferred Examples of aromatic polyols are hydroquinone, 4,4'-dihydroxybiphenyl, 2,2-di(4-hydroxyphenyl)propane, and also novolaks and resols. Examples of polyepoxides are those

based on the aforementioned polyols, especially the aromatic polyols, and epichlorhydrin. Further suitable polyols include polymers and copolymers containing hydroxyl groups in the polymer chain or in side groups, such as polyvinyl alcohol and copolymers thereof or polyhydroxyalkyl methacrylates or copolymers thereof, for example. Oligoesters containing hydroxyl end groups are further suitable polyols.

Examples of aliphatic and cycloaliphatic polyols are alkylene diols having preferably from 2 to 12 carbon atoms, such as ethylene glycol, 1,2- or 1,3-propanediol, 1,2-, 1,3- or 1,4-butanediol, pentanediol, hexanediol, octanediol, dodecanediol, diethylene glycol, triethylene glycol, polyethylene glycols having molecular weights of preferably from 200 to 1500, 1,3-cyclopentanediol, 1,2-, 1,3- or 1,4-cyclohexanediol, 1,4-dihydroxymethylcyclohexane, glycerol, tris(β -hydroxyethyl)amine, trimethylolethane, trimethylolpropane, pentaerythritol, dipentaerythritol and sorbitol.

The polyols may have been partly or fully esterified with one or more different unsaturated carboxylic acids, the free hydroxyl groups in partial esters possibly having been modified, e.g. etherified or esterified with other carboxylic acids. Examples of such esters are for example trimethylolpropane triacrylate, trimethylolethane triacrylate, trimethylolpropane trimethacrylate, trimethylolethane trimethacrylate, tetramethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol diacrylate, pentaerythritol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol diacrylate, dipentaerythritol triacrylate, dipentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate, tripentaerythritol octaacrylate, pentaerythritol dimethacrylate, pentaerythritol trimethacrylate, dipentaerythritol dimethacrylate, dipentaerythritol tetramethacrylate, tripentaerythritol octamethacrylate, pentaerythritol diitaconate, dipentaerythritol trisitaconate, dipentaerythritol pentaitaconate, dipentaerythritol hexaitaconate, ethylene glycol diacrylate, 1,3-butanediol diacrylate, 1,3-butanediol dimethacrylate, 1,4-butanediol diitaconate, sorbitol triacrylate, sorbitol tetraacrylate, modified pentaerythritol triacrylate, sorbitol tetramethacrylate, sorbitol pentaacrylate, sorbitol hexaacrylate, oligoester acrylates and methacrylates, glycerol diacrylate and triacrylate, 1,4-cyclohexane diacrylate, bisacrylates and bismethacrylates of polyethylene glycol having a molecular weight from 200 to 1500, or mixtures thereof.

Suitable UV-curable resins include the amides of identical or different unsaturated carboxylic acids with aromatic, cycloaliphatic and aliphatic polyamines having preferably from 2 to 6, particularly from 2 to 4 amino groups. Examples of such polyamines are ethylenediamine, 1,2- or 1,3-propylenediamine, 1,2-, 1,3- or 1,4-butylenediamine, 1,5-pentylenediamine, 1,6-hexylenediamine, octylenediamine, dodecylenediamine, 1,4-diaminocyclohexane, isophoronediamine, phenylenediamine, bisphenylenediamine, di- β -aminoethyl ether, diethylenetriamine, triethylenetetramine, di(β -aminoethoxy)- or di(β -aminopropoxy)ethane. Further suitable polyamines are polymers and copolymers containing possibly additional amino groups in the side chain, and oligoamides having amino end groups. Examples of such unsaturated amides are: methylenebisacrylamide, 1,6-hexamethylenebisacrylamide, diethylenetriaminetrismethacrylamide, bis(methacrylamidopropoxy)ethane, β -methacrylamidoethyl methacrylate, and N-[(β -hydroxyethoxy)ethyl]acrylamide.

Suitable unsaturated polyesters and polyamides are derived, for example, from maleic acid and diols or diamines. The maleic acid may have been replaced in part by other dicarboxylic acids. They may be used together with ethylenically unsaturated comonomers, e.g. styrene. The polyesters and polyamides may also be derived from dicarboxylic acids and ethylenically unsaturated diols or diamines, especially from relatively long chain ones having, for example, from 6 to 20 carbon atoms. Examples of polyurethanes are those synthesized from saturated or unsaturated diisocyanates and unsaturated or saturated diols, respectively.

Polybutadiene and polyisoprene and copolymers thereof are known. Examples of suitable comonomers are olefins such as ethylene, propene, butene, hexene, (meth)acrylates, acrylonitrile, styrene or vinyl chloride. Polymers containing (meth)acrylate groups in the side chain are likewise known. They may comprise, for example, reaction products of novolak-based epoxy resins with (meth)acrylic acid, homopolymers or copolymers of vinyl alcohol or the hydroxyalkyl derivatives thereof that have been esterified with (meth)acrylic acid, or homopolymers and copolymers of (meth)acrylates esterified with hydroxyalkyl (meth)acrylates.

The UV-curable resins may be used alone or in any desired mixtures. Preference is given to using mixtures of polyol (meth)acrylates.

It is also possible to add binders to the compositions of the invention, which is especially appropriate when the photopolymerizable compounds are liquid or viscous substances. The amount of the binder can be for example 5-95, preferably 10-90 and especially 40-90% by weight, based on the overall solids. The choice of binder is made depending on the field of use and the properties required for that field, such as developability in aqueous and organic solvent systems, adhesion to substrates, and oxygen sensitivity, for example.

The unsaturated compounds may also be used in a mixture with non-photopolymerizable film-forming components. These may be, for example, physically drying polymers or their solutions in organic solvents, such as nitrocellulose or cellulose acetobutyrate, for example. They may also, however, be chemically and/or thermally curable resins, such as polyisocyanates, polyepoxides or melamine resins, for example. By melamine resins are meant not only condensates of melamine (1,3,5-triazine-2,4,6-triamine) but also those of melamine derivatives. In general, the components comprise a film-forming binder based on a thermoplastic or thermosettable resin, predominantly on a thermosettable resin. Examples thereof are alkyd, acrylic, polyester, phenolic, melamine, epoxy and polyurethane resins and mixtures thereof. The additional use of thermally curable resins is of importance for use in what are known as hybrid systems, which may be both photopolymerized and also thermally crosslinked.

Component (a) may comprise, for example, a coating composition comprising (a1) compounds containing one or more free-radically polymerizable double bonds and further containing at least one other functional group which is reactive in the sense of an addition reaction and/or condensation reaction (examples have been given above), (a2) compounds containing one or more free-radically polymerizable double bonds and further containing at least one other functional group which is reactive in a sense of an addition reaction and/or condensation reaction, the additional reactive functional group being complementary to or reactive toward the additional reactive functional groups of component (a1), (a3) if desired, at least one monomeric, oligomeric and/or polymeric compound containing at least one functional group which is reactive in the sense of an addition reaction and/or condensation reaction toward the functional groups from component (a1) or component (a2) that are present in addition to the free-radically polymerizable double bonds.

Component (a2) carries in each case the groups which are reactive toward or complementary to component (a1). In this context it is possible in each case for different kinds of functional groups to be present in one component. In component (a3) there is a further component available containing functional groups which are reactive in the sense of addition reactions and/or condensation reactions and which are able to react with the functional groups of (a1) or (a2) that are present in addition to the free-radically polymerizable double bonds. Component (a3) contains no free-radically polymerizable double bonds. Examples of such combinations of (a1), (a2), (a3) can be found in WO-A-99/55785. Examples of suitable reactive functional groups are selected, for example, from hydroxyl, isocyanate, epoxide, anhydride, carboxyl or blocked amino groups. Examples have been described above.

The coating compositions may additionally comprise one or more components taken, for example, from the group consisting of pigments, dyes, fillers, flow control agents, dispersants, thixotropic agents, adhesion promoters, antioxidants, light stabilizers and curing catalysts.

The pigments are, for example, titanium dioxide, iron oxide, aluminium bronze or phthalocyanine blue.

Examples of fillers are talc, alumina, aluminium silicate, barytes, mica, and silica.

Flow control agents and thixotropic agents are based, for example, on modified bentonites.

Adhesion promoters are based, for example, on modified silanes.

Suitable curing catalysts are for example photoinitiators. Photoinitiators suitable for use in the process according to the invention are in principle any compounds and mixtures that form one or more free radicals when irradiated with electromagnetic waves. These include initiator systems consisting of a plurality of initiators and systems that function independently of one another or synergistically. In addition to coinitiators, for example amines, thiols, borates, enolates, phosphines, carboxylates and imidazoles, it is also possible to use sensitizers, for example acridines, xanthenes, thiazenes, coumarins, thioxanthenes, triazines and dyes. A description of such compounds and initiator systems can be found e.g. in Crivello J.V., Dietliker K.K., (1999): Chemistry & Technology of UV & EB Formulation for Coatings,

Inks & Paints, and in Bradley G. (ed.) Vol. 3: Photoinitiators for Free Radical and Cationic Polymerisation 2nd Edition, John Wiley & Son Ltd. Such compounds and derivatives are derived, for example, from the following classes of compounds: benzoin, benzil ketals, benzophenones, acetophenones, hydroxyalkylphenones, aminoalkylphenones, acylphosphine oxides, bisacylphosphine oxides, acylphosphine sulfides, bisacylphosphine sulfides, acyloxyiminoketones, alkylamino-substituted ketones, such as Michler's ketone, peroxy compounds, dinitrile compounds, halogenated acetophenones, phenylglyoxylates, dimeric phenylglyoxalates, benzophenones, oximes and oxime esters, thioxanthenes, coumarins, ferrocenes, titanocenes, onium salts, sulfonium salts, iodonium salts, diazonium salts, borates, triazines, bisimidazoles, polysilanes and dyes. It is also possible to use combinations of the compounds from the mentioned classes of compounds with one another and combinations with corresponding coinitiator systems and/or sensitizers.

Of special interest is a coating composition wherein the solid content of component (b) is present in an amount of from 0.01 to 20 %, preferably from 0.05 to 5% by weight, in particular from 0.1 to 5% by weight, based on the weight of the overall solids content of the coating composition.

The present invention relates also to a process for the preparation of a coating composition, which comprises mixing the first component (a) with component (b); distillation of the solvent under normal pressure at a temperature range of 50 to 140°C till most or all of the solvent is evaporated; and optionally, adding the second component (a).

Of special interest is a process for the preparation of a coating composition wherein the first component (a) is a polyol and the second component (a) is a polyisocyanate; or the first component (a) is a polyacrylate and the second component (a) is melamine.

The coating materials can be applied to the substrate by the customary techniques, for example by spraying, dipping, spreading or electrodeposition. In many cases, a plurality of coats are applied. Depending on whether the binder is a physically, chemically or oxidatively drying resin or a heat-curing or radiation-curing resin, the coating is cured at room temperature or by heating (stoving) or by irradiation.

The coating material is preferably a clearcoat or topcoat for metallic substrates such as, for example, iron, steel, copper, zinc or aluminium, and alloys thereof; plastics; or automotive substrates.

Also of interest are multi-component composite coating compositions which comprise a basecoat deposited from a pigmented coating composition, and any one of the foregoing cured compositions according to the present invention formed as topcoat over the basecoat.

Component (b) has additionally the advantage that it favourably affect the adhesion between coating and metal, shows no adverse effects on the storage stability of the novel coating compositions, and exhibit good compatibility with the binder.

A preferred embodiment of the present invention is therefore the use of component (b) as reinforcer of coatings and improver of scratch resistance in coating compositions for surfaces.

The present invention also relates to a process for protecting a substrate, which comprises applying thereto a coating composition comprising components (a) and (b) and then drying and/or curing it.

The present invention likewise relates to a process for preparing a reinforced coating with improved scratch resistance on a surface, which comprises treating this surface with a coating composition comprising components (a) and (b), and then drying and/or curing it.

The examples, which follow, illustrate the invention in more detail. Parts and percentages are by weight.

Example 1: Preparation of Sol 101.

a) Preparation of a polyol component P1.

54.8 g of Macrynal SM 510n (60% supply form from Solutia), 11.5 g of butylglycol acetate, 4.70 g of Solvesso 100 (obtained from Exxon), 5.68 g of Methyl isobutyl ketone, 0.07 g of

zinc octoate and 0.15 g of BYK 300 (Byk-Chemie, Germany, anti-foaming agent) is mixed to give 76.9 of the polyol component P1.

b) Preparation of Sol 101.

64.6 g of tetraethoxysilane (Fluka AG, Switzerland) is diluted with methanol to a total volume of 500 ml. The clear solution is added simultaneously with a solution of 12.5 g of ammonia and 37.5 g of water both dissolved in totally 500 ml of methanol into a 1l round bottom flask. The solution is stirred for two hours. After this time dynamic light scattering indicates a particle size of 23 nm. 21.55 g of this solution is added to 29.98 g of the polyol component P1 prepared according to Example 1a and thoroughly mixed by stirring. The mixture is concentrated by distillation of volatiles to a final weight of 28.06 g of Sol 101 with 35.8% of residual solids.

Example 2: Preparation of Sol 102.

3.17 g of the methanolic solution prepared according to Example 1b is added to 30.02 g of the polyol component P1 prepared according to Example 1a and thoroughly mixed by stirring. The mixture is concentrated by distillation of volatiles to a final weight of 30.78 g of Sol 102 with 40.6% residual solids.

Example 3: Preparation of Sol 103.

11.2 g of tetraethoxysilane (Fluka AG, Switzerland) is diluted with ethanol to a total volume of 90 ml. The clear solution is added simultaneously with a solution of 2.59 g of ammonia and 7.77 g of water both dissolved in totally 90 ml ethanol into a 250ml round bottom flask. The solution is stirred for 5 hours. After this time dynamic light scattering/transmission electron microscopy indicates a particle size of 100 nm. 60.05 g of this solution is added to 51.30 g of the polyol component P1 prepared according to Example 1a and thoroughly mixed by stirring. The mixture is concentrated by evaporation at 42°C at 225 mmbar to a give 56.68 g of Sol 103 with 49.8% residual solids.

Example 4: Preparation of Sol 104.

27.50 g of tetraethoxysilane (Fluka AG, Switzerland) is diluted with methanol to a total volume of 250 ml. The clear solution is added simultaneously with a solution of 8.75 g of ammonia and 26.25 g of water both dissolved in a total of 250 ml of methanol into a 500 ml round bottom flask. The solution is stirred for 2 hours. After this time dynamic light scattering indicates a particle size of 162 nm. 3.43 g of this solution is added to 40.04 g of the polyol component P1 prepared according to Example 1a and mixed thoroughly by stirring. The weight of this mixture is adjusted by distillation of volatiles to give 25.75 g of Sol 104 with 43.1% residual solids.

Example 5: Preparation of Sol 105 (MA 37.3).

1.2 Liter of ethanol and 70 ml of aqueous ammonia (25%) are mixed in a 1.5 liter flask and stirred for 5 minutes. Then 167.1 g (180 ml) of tetraethoxysilane is added at once and the solution is stirred for 2 days at ambient temperature. One liter of this solution is transferred to another 1.5 liter flask and 31.35 g (30 ml) of 3-methacryloyloxypropyl-trimethoxysilane (Silan A174, Fluka, purum) added at once and stirred for 1 hour. Nitrogen is bubbled through this "sol" first at room temperature during two hours and then at 75°C until the volume of the sol decreased to ca. 250 ml. 100 ml of hexane is added and the white precipitate isolated by centrifugation (2000 rpm, 7 min.). The precipitate is purified by re-suspension in a mixture of 100 ml of hexane and 30 ml of ethanol and isolated by centrifugation as above. 50 ml of n-butyl acetate is added and the mixture is vigorously shaken for 2 hours until a homogeneous, stable, slightly opaque dispersion of silica nanoparticles is obtained. The particle size is 132 nm, as determined by transmission electron microscopy (TEM) and the solid content is 35 wt.%.

Example 6: Scratch resistance of polyurethane coatings.

A specific amount (see Table 1) of Sols 101 - 104 as prepared according to Examples 1 - 4 are treated with 2.31 g of Desmodur N 75 (RTM) (Isocyanate from Bayer). The resulting clear coat formulation (solids content 50%) is subsequently applied as transparent topcoat at a dry film thickness of 40µm onto aluminium panels (10 cm x 30 cm) precoated with a black basecoat. After application, the clear coat is cured at 80°C for 45 minutes.

The scratch resistance of the coated panels is measured using the following method: The 20° gloss of the panels is measured 48 hours after curing (DIN 67 530). The panels are subsequently exposed to scratching by an Amtec Kistler apparatus for the number of cycles as indicated in Table 1. The 20° gloss is measured again on the scratched area of each test panel. The results are summarized in Table 1.

Table 1:

Example	Sol	wt.-% silica	particle size (nm)	initial gloss	gloss after 10 cycles	gloss after 20 cycles
6a ^{a)}	—	—	—	83	57	34
6b ^{b)}	7.80 g 101	3.7	23	91	n.m. ^{c)}	40
6c ^{b)}	8.57 g 102	0.53	23	90	69	49
6d ^{b)}	7.20 g 103	13.5	100	74	62	54
6e ^{b)}	7.70 g 104	0.52	162	89	73	69

- a) Comparison Example.
b) Example according to the invention.
c) not measured.

Example 7: Scratch resistance of a UV-curable coating.

A specific amount (see Table 3) of Sol 105 as prepared according to Example 5 was added to 50 g of the resin mixture according to Table 2.

Table 2:

parts by weight	Resin
57.3	Ebecryl 284 (RTM) ^{a)}
41.4	Roskydal UA VP LS2308 (RTM) ^{b)}
1.3	Glide 100(RTM) ^{c)}
0.3	Irgacure 184 (RTM) ^{d)}

- a) Ebecryl 284 (RTM) (UCB Chemicals) contains 88 parts of aliphatic urethaneacrylate and 12 parts of hexaneoldiacrylate.
b) Roskydal UA VP LS2308 (RTM) (Bayer AG) is a aliphatic urethane tri/tetraacrylate.
c) Glide 100 (RTM) (Tego Chemicals) is a flow agent.

- d) Irgacure 184 (RTM) (Ciba Specialty Chemicals Inc.) is an α -hydroxyketone photoinitiator.

The resulting clear coat formulation which contains 20 wt% silica was subsequently applied as transparent topcoat at a dry film thickness of 40 μ m onto aluminium panels (10cm x 30 cm) precoated with a black basecoat. After application, the solvent was flashed off at 80°C during 10 minutes in an oven. The clear coat is cured under two mercury medium pressure lamps with 120 W/cm each with a conveyor belt speed of 5 m/minute.

The scratch resistance of the coated panels were measured in analogy to Example 6. The results are summarized in Table 3.

Table 3:

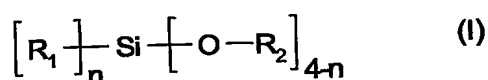
Example	Sol	wt.-% silica	particle size (nm)	initial gloss	gloss after 10 cycles	gloss after 20 cycles
7a ^{a)}	—	—	—	86	71	44
7b ^{b)}	11.8 g 105	20	132	86	74	47

- a) Comparison Example.
b) Example according to the invention.

What is claimed is:

1. A coating composition comprising

- a) an organic film-forming binder, and
- b) an inorganic additive of small particle size dispersed in an aqueous or alcoholic solvent prepared by a process which comprises the hydrolysis of a metal alcoholate, metal halide or a compound of the formula I



in which

R₁ is C₁-C₈alkyl, C₅-C₈cycloalkyl, phenyl or C₁-C₄alkyl substituted phenyl;

R₂ is C₁-C₈alkyl, and

n is 0, 1, 2 or 3; with a base.

2. A coating composition according to claim 1, wherein the coating is transparent.

3. A coating composition according to claim 1, in which the metal is beryllium, aluminium, titanium, chromium, iron, zinc, zirconium, niobium or cerium.

4. A coating composition according to claim 1, in which the alcoholic solvent is methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol or tert-butanol.

5. A coating composition according to claim 1, in which the base is an amine of the formula II



wherein

R₃, R₄ and R₅ independently of one another are hydrogen or C₁-C₈alkyl.

6. A coating composition according to claim 1, in which the particle size of the inorganic additive is in the range of from 2 to 300 nanometre.
7. A coating composition according to claim 1, wherein the hydrolysis takes place at a temperature of from -20 to 80°C.
8. A coating composition according to claim 1, in which n is 0.
9. A coating composition according to claim 1, in which component (b) is a hydrolyzed compound of the formula I wherein, R₂ is ethyl and n is 0, with aqueous ammonia.
10. A coating composition according to claim 1, wherein the coating composition is a paint.
11. A coating composition according to claim 1, wherein the coating composition is an aqueous paint.
12. A coating composition according to claim 1, wherein component (a) is an epoxy resin, a polyurethane resin, an amino resin, an acrylic resin, an acrylic copolymer resin, a polyvinyl resin, a phenolic resin, a styrene/butadiene copolymer resin, a vinyl/acrylic copolymer resin, a polyester resin, a UV-curable resin, an alkyd resin or a mixture of two or more of these resins or an aqueous basic or acidic dispersion of these resins or mixtures of these resins or an aqueous emulsion of these resins or mixtures of these resins.
13. A coating composition according to claim 1, additionally comprising one or more components taken from the class consisting of pigments, dyes, fillers, flow control agents, dispersants, thixotropic agents, adhesion promoters, antioxidants, light stabilizers and curing catalysts.
14. A coating composition according to claim 1, wherein the solid content of component (b) is present in an amount of from 0.01 to 20 % based on the weight of the overall solids content of the coating composition.

15. A process for the preparation of a coating composition according to claim 1, which comprises mixing the first component (a) with component (b); distillation of the solvent under normal pressure at a temperature range of 50 to 140°C til most or all of the solvent is evaporated; and optionally, adding the second component (a).

16. A process according to claim 15, wherein the first component (a) is a polyol and the second component (a) is a polyisocyanate; or the first component (a) is a polyacrylate and the second component (a) is melamine.

17. A process for protecting a substrate, which comprises applying thereto a coating composition according to claim 1 and then drying and/or curing it.

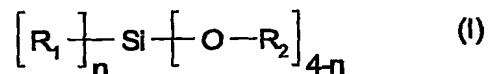
18. A process for preparing a reinforced coating with improved scratch resistance on a surface, which comprises treating this surface with a coating composition according to claim 1 and then drying and/or curing it.

19. The use of the component (b) as defined in claim 1 as reinforcer of coatings and improver of scratch resistance in coating compositions for surfaces.

Abstract

The instant invention discloses a coating composition comprising

- a) an organic film-forming binder, and
- b) an inorganic additive of small particle size dispersed in an aqueous or alcoholic solvent prepared by a process which comprises the hydrolysis of a metal alcoholate or a compound of the formula I



in which

R₁ is C₁-C₈alkyl, C₅-C₈cycloalkyl, phenyl or C₁-C₄alkyl substituted phenyl;

R₂ is C₁-C₈alkyl, and

n is 0, 1, 2 or 3; with a base.

These coatings for protecting surfaces are reinforced and show improved scratch resistance.

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